UCRL- 90545 Rev. I
PREPRINT

The Potentiometric Titration of Gold, Platinum, and Some Other Precious Metals with Cetylpyridinium Chloride

Walter S. Selig

This paper was prepared for submittal
to
Fresenius Z. Anal. Chem.

May 1984

Lawrence Livermore National Laboratory

The Potentiometric Titration of Gold, Platinum, and Some Other Precious Metals with Cetylpyridinium Chloride

Walter S. Selig
Lawrence Livermore National Laboratory, University of California,
P. O. 808, Livermore, CA 94550, U.S.A.

SUMMARY. The precipitation titration of some precious metal halides vs cetylpyridinium chloride was investigated, with emphasis on tetrachloroaurate and hexachloroplatinate. The optimum pH for titration of the latter anions was from 0.5 to 1.0. Differentiation of $AuCl_4^-$ and $PtCl_6^{2-}$ with this titrant is not feasible; their sum can, however, be determined. Titration vs tetraphenylarsonium chloride at the same pH is successful only for $AuCl_4^-$ which can, thus, be determined in the presence of $PtCl_6^{2-}$. Tetrachlororuthenate(IV), hexachlororhodate(III) and hexachloriridate(III) did not yield analytically useful titration curves. Hexachloroosmate(IV), tetrachloropalladate(II), hexachloropalladate(IV), hexachloroiridate(IV) and tetrachlorplatinite(II) gave good titration curves.

We have previously used quaternary ammonium halides as titrants for various organic and inorganic anions. Some precious metal halides ($AuCl_4^-$, $PdCl_4^{2-}$, $PtCl_6^{2-}$, and $IrCl_6^{3-}$) were determined using cetyltrimethylammonium bromide as titrant [8]. Subsequently, we found cetylpyridinium chloride (CPC) to be a superior titrant because of its higher solubility in water and have used it routinely. This work has been summarized in a review in this journal [9]. In this paper, we report the optimum conditions for the titrimetric determination of milligram amounts of gold as $AuCl_4^-$ and platinum as $PtCl_6^{2-}$. Some other precious metal halides will also be discussed. While Au(III) and Pt(IV) can be determined in the same solution using two different titrants, no effort has been made to selectively titrate any of the other precious metal chlorides.

EXPERIMENTAL

The sensing electrode was a spectrographic graphite rod coated with a solution of poly(vinyl chloride) and dioctylphthalate in tetrahydrofuran as previously described [10,13]. The reference electrode was a double-junction Ag/AgCl electrode (Orion No. 90-01) with a 0.1 M sodium nitrate salt-bridge. The titration system was controlled by a Tektronix 4051 graphics computer system which has previously been described [7]. Titration rates were kept constant at 0.3 ml/min. Stirring was provided by a magnetic stirrer. The stirring motor was isolated from the titration vessel by a water cooling plate and by a grounded aluminum plate. Titrations were performed at 23 ± 1°C.

The titrant was aqueous 0.01 M cetylpyridinium chloride (CPC) prepared from the monohydrate. The primary standard was a gold solution prepared from Wildberg gold wire, of >99.995% purity and assayed by a controlled-potential coulometric method [3,4]. The wire was washed in nitric acid, dissolved in aqua regia and the solution diluted to volume with distilled water. Approximately 0.005 N solutions (with respect to the titrant) of the ions were investigated. The compounds used, and the acids used in the preparation of solutions are summarized in Table 1. All compounds were of high purity. Aliquots were pipetted into 50-ml beakers containing a Teflon-coated stirring bar. The solutions containing Au(III) and Pt(IV) were adjusted to pH 0.5 to 1 with hydrochloric acid using a pH meter and diluted to 25 ml prior to titration. Titration endpoints were calculated as previously described [12].

RESULTS AND DISCUSSION

Simple titrimetric methods were required in our Laboratory for the analysis of milligram amounts of either platinum or gold in highly acid solutions. We routinely employ controlled-potential coulometry for the determination of gold in this range (3,4), but there is no comparable method for platinum. We have surveyed also several other precious metals in this study. According to Beamish and Van Loon [2], there is a marked deficiency of acceptable volumetric methods for most of the platinum metals. In addition, many of the volumetric methods are useful only when applied to the isolated platinum metal constituent under carefully controlled conditions.

Quaternary ammonium halides were previously used by us to determine a large variety of inorganic and organic anions [9]. In a previous paper [8] we have surveyed, among a large variety of inorganic anions, the volumetric determination of several precious metal halides using cetyltrimethylammonium bromide. CPC, however, is now our reagent of choice because of its higher solubility in aqueous solution.

The analytical reactions for Au(III) and Pt(IV) are shown in equations (1) and (2):

$$C_{21}H_{38}N^{+} + AuCl_4^{-} \longrightarrow (C_{21}H_{38}N)AuCl_4 \qquad (1)$$

$$2C_{21}H_{38}N^{+} + PtCl_6^{2-} \longrightarrow (C_{21}H_{38}N)_2PtCl_6 \qquad (2)$$

where $C_{21}H_{38}N^{+}$ is the cetylpyridinium cation.

We previously used a variety of commercially available ion-selective electrodes (ISE's) as sensors in titrations with quaternary ammonium halides [8]. We later found that inexpensive "home-made" sensors can be used with superior results [10,13]. For this purpose, we recommend spectroscopic graphite rods coated with a solution of poly(vinyl chloride) and dioctylphthalate in tetrahydrofuran. Other coating solutions have also been discussed [11]. Unlike the liquid-membrane ISE's, these sensors are practically indestructible. When their response deteriorates, the organic coating can easily be replaced.

The titrant was standardized vs the primary standard gold solution. The mean normality was 0.01022, with a standard deviation of 0.00002 for nine replicates. A typical titration curve for 0.025 mmol of Au(III) is shown in Figure 1. Statistics for the recoveries of 1 to 10 mg of Pt(IV) are shown in Table 2. The mean recovery over the entire range was 100.16%, with a pooled standard deviation of 0.34% for 36 replicates. While CPC cannot differentiate between Au(III) and Pt(IV), several experiments indicated that their sum was accurately determined with a mean recovery of 99.9%.

Willard and Smith [15] have discussed the use of tetraphenylarsonium chloride for the gravimetric determination of various anions. Platinum(IV) and Au(III), which form halide complexes, also are precipitated by this reagent. Neeb has used tetraphenylarsonium chloride and benzyltriphenylphosphonium chloride in the presence of an excess of chloride ions for the gravimetric determination of osmium(IV) [5] and of iridium(IV) [6]. Baczuk and DuBois [1] first used tetraphenylarsonium chloride as a titrant (rather than a precipitant) for perchlorate, monitoring the titration with a perchlorate ISE. We found that with our electrodes tetraphenylarsonium chloride reacts stoichiometrically at pH 0.5-1 with Au(III) according to the reaction

$$(C_6H_5)_4As^+ + AuCl_4^- \longrightarrow [(C_6H_5)_4As]AuCl_4 \qquad (3)$$

but it does not react at all with Pt(IV). In solutions containing both ions, only Au(III) is titrated. This makes the titration of Au(III) and Pt(IV) in the same solution possible. The sum of the two ions is determined by titration vs CPC in one aliquot, while Au(III) alone is determined by titration vs tetraphenylarsonium chloride in another aliquot.

Table 3 lists the optimum pH, feasible pH ranges, and quality of the titration curves (as judged from their magnitude and steepness) for $AuCl_4^-$ and $PtCl_6^{2-}$, (which were of primary interest to us), as well as of some other precious metal chlorides. Some comments on the results follow:

(1) Aqueous solutions of $PtCl_4^{2-}$ were unstable; the volumes of CPC required for consecutive aliquots of the same solution decreased continuously. In 10% HCl, however, stable recoveries were obtained.

(2) No analytically useful results were obtained for $IrCl_6^{3-}$ and tetrachlororuthenate. The titration curves were small and quite shallow. Hexachlororhodate(III) solutions were unstable both in aqueous solution and dilute HCl and thus, could not be analyzed by our method.

(3) $OsCl_6^{2-}$, $PdCl_4^{2-}$, $IrCl_6^{2-}$, and $PdCl_6^{2-}$ yielded good titration curves.

(4) While $PdCl_6^{2-}$ could be satisfactorily titrated vs CPC, the resulting precipitate was of the same elemental composition as that for $PdCl_4^{2-}$. This was confirmed by x-ray diffraction patterns. It seems that in the titration the tetravalent Pd is reduced to the more stable divalent state.

Some of the cetylpyridinium salts (as well as the tetraphenylarsonium salt of $AuCl_4^-$) were isolated by filtration, washing with water, and air-drying. The iridium salts could not be isolated by filtration. Analytical data for the recovered precipitates are shown in Table 4. The agreement between the calculated and found values is quite good, confirming the postulated stoichiometry of the reactions.

Westland and Westland [14] carried out a critical study of the determination of platinum by precipitation with dimethylbenzylphenylammonium chloride, a quaternary ammonium compound similar to CPC. While this compound probably can also be used for the titrimetric determination of the compounds discussed, it has a lower molecular weight than CPC, and is thus expected to yield precipitates of higher solubility. The compound also costs three times as much as CPC.

$PdCl_4^{2-}$ and $PtCl_4^{2-}$ at their optimum pH values for titrations vs CPC (see Table 3) did not form precipitates with tetraphenylarsonium chloride. It is, therefore, likely that $AuCl_4^-$ can be determined in their presence. Attempts to determine $KAu(CN)_2$ by direct titration vs CPC failed: very poor titration curves were obtained in the presence of excess of cyanide. The resulting precipitate, however, conformed in composition to the expected cetylpyridinium dicyanoaurate(I), as shown in Table 4. Similarly, with tetraphenylarsonium chloride in the presence of excess cyanide very poor titration curves were obtained. The precipitate, however, was the expected tetraphenylarsonium-dicyanoaurate(I). It is noteworthy that gold in these precipitates is present in the monovalent state. Successful titration vs CPC required conversion of the monovalent gold to $AuCl_4^-$ by heating with aqua regia. $Pt(CN)_2$, however, could be titrated successfully with CPC in the presence of excess of cyanide. The reactions are

$$Pt(CN)_2 + 2CN^- \longrightarrow Pt(CN)_4^{2-} \tag{4}$$

$$Pt(CN)_4^{2-} + 2C_{21}H_{38}N^+ \longrightarrow (C_{21}H_{38}N)_2Pt(CN)_4 \tag{5}$$

A 150-fold excess of cyanide yielded the best titration curves. However, these curves were not as steep as those obtained in hydrochloric acid solutions. Di(cetylpyridinium)tetracyanoplatinite(II) was isolated as the monohydrate according to elemental analysis, which was confirmed by thermogravimetric analysis. Palladium(II) in the presence of excess cyanide yielded a break which was not analytically useful. The resulting di(cetylpyridinium)tetracyanopalladite(II) was the dihydrate according to elemental analysis, also confirmed by thermogravimetric analysis. Any cation capable of forming a chloride complex is expected to interfere in the titration of precious metal halides vs CPC, but for single-component solutions, the titrant is quite useful.

ACKNOWLEDGMENT

The writer thanks Carol M. Weaver for the X-ray powder patterns, Lewis J. Gregory and Randy E. Benson for the elemental analyses and Glendon L. Crossman for the thermogravimetric analyses.

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

REFERENCES

1. Baczuk RJ, DuBois RJ (1968) Anal Chem 40:685
2. Beamish FE, Van Loon JC (1977) Analysis of Noble Metals. Academic Press, New York
3. Harrar JE, Stephens FB (1962) J Electroanal Chem 3:112
4. Harrar JE, Waggoner MC (1981) Plating Surf Fin 68:41
5. Neeb R (1960) Fresenius Z Anal Chem 177:20
6. Neeb R (1960) Fresenius Z Anal Chem 177:420
7. Selig W (1978 II) Mikrochim Acta 75
8. Selig W (1979 II) Mikrochim Acta 373
9. Selig W (1982) Fresenius Z Anal Chem 312:419
10. Selig W (1982) Anal Letters 15:309
11. Selig W (1983 I) Mikrochim Acta 333
12. Selig WS (1984) Fresenius Z Anal Chem 317:131
13. Selig WS (1984) J Chem Educ 61:80
14. Westland AD, Westland L (1960) Talanta 3:364
15. Willard HH, Smith GM (1939) Ind Eng Chem Anal Ed 11:186, 269

FIGURE CAPTION

Fig. 1 Titration curve of 0.025 mmol of $AuCl_4^-$ vs 0.01 M CPC at pH 0.5.

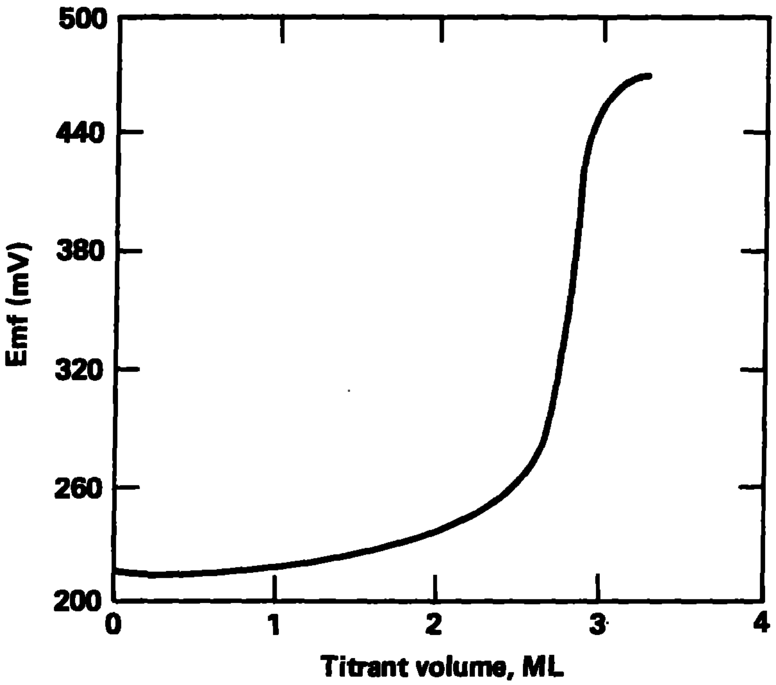
500
440
380
320
260
200
0
1
2
3
4
Emf (mV)
Titrant volume, ML

Table 1. Compounds and solutions used

Element(valence)	Compound used	Acids used for solution	Remarks
Pt(IV)	K_2PtCl_6	10% CHl + 3.3% HNO_3	
Pt(II)	$(NH_4)_2PtCl_4$	10% HCl	soluble in water
Au(III)	$KAuCl_4 \cdot 2H_2O$	10% HCl + 3.3% HNO_3	
Au(III)	Au wire, Wildberg	10% HCl + 3.3% HNO_3	
Pd(IV)	K_2PdCl_6	10% HCl + 3.3% HNO_3	
Pd(II)	Na_2PdCl_4	none	soluble in water
Os(IV)	K_2OsCl_6	10% HCl	
Ir(III)	$K_3IrCl_6 \cdot H_2O$	none	soluble in water
Ir(IV)	K_2IrCl_6	none	soluble in water
Ru(IV)	$K_4Ru_2Cl_{10} \cdot H_2O$	10% HCl	
Rh(III)	$(NH_4)_3RhCl_6$	none	soluble in water

Table 2. Statistics for the recovery of platinum as K_2PtCl_6 (99.9%)

Taken, mg Pt	Recovered, mg Pt (standard deviation)	Recovered, % (standard deviation)	Number of replicates
0.969	0.985 (0.005)	101.69 (0.52)	7
2.422	2.422 (0.007)	99.99 (0.29)	7
3.875	3.846 (0.004)	99.26 (0.10)	5
4.843	4.855 (0.035)	100.25 (0.74)	6
7.265	7.273 (0.014)	100.11 (0.19)	6
9.687	9.602 (0.010)	99.12 (0.11)	5

Table 3. Summary of conditions and results for various precious metal chlorides

Ion determined	Optimum pH range	Feasible pH range	Quality of titration curve	Remarks
$AuCl_4^-$	0.5 - 1	<0 - 5	very good	at pH >2 curve has 2 inflections
$PtCl_6^{2-}$	0.5	<0 - 2	very good	at pH >2 curve has 2 inflections
$PtCl_4^{2-}$	1.15		very good	in aqueous solution rapid oxidation occurs
$PdCl_4^{2-}$	1 - 2	0.65 - 4.1	very good	
$PdCl_6^{2-}$	0.5 - 1	0.15 - 4.1	good	ppt. reduced to Pd^{+2}
$OsCl_6^{2-}$	0.5 - 1	0 - 6.3	very good	
$IrCl_6^{3-}$	5.5 - 8	1.8 - 10	very poor	not analytically useful, breaks too shallow
$IrCl_6^{2-}$	3 - 7	0.8 - 7	very good	
$Ru_2Cl_{10}^{4-}$	1.7 - 2.4		poor	not analytically useful, breaks too shallow
$RhCl_6^{3-}$	1.8 - 2.1		fair	not analytically useful, rapid decomposition

Table 4. Analysis of precipitated reaction products

Compound	Calculated, percent C	H	N	Found, percent C	H	N
$(C_{21}H_{38}N)AuCl_4$	39.21	5.95	2.18	39.43	5.93	2.18
$(C_{21}H_{38}N)_2PtCl_6$	49.61	7.53	2.75	50.10	7.57	2.77
$(C_{21}H_{38}N)_2PtCl_4$	53.33	8.10	2.96	53.50	8.26	2.99
$(C_{21}H_{38}N)_2OsCl_6$	49.85	7.57	2.77	50.16	7.42	2.76
$(C_{21}H_{38}N)_2PdCl_4$	58.85	8.94	3.27	58.74	8.85	3.24
$(C_{21}H_{38}N)_2RuCl_6$	54.66	8.30	3.04	54.90	8.34	3.11
$[(C_6H_5)_4As]AuCl_4$	39.92	2.79	-	39.89	2.84	-
$(C_{21}H_{38}N)_2Pt(CN)_4 \cdot H_2O$	59.64	8.49	9.07	59.74	8.35	8.54
$(C_{21}H_{38}N)_2Pd(CN)_4 \cdot 2H_2O$	66.46	8.92	9.30	66.05	9.19	9.40
$(C_{21}H_{38}N)Au(CN)_2$	49.91	6.92	7.59	49.89	6.90	7.25
$[(C_6H_5)_4As]Au(CN)_2$	49.38	3.19	4.43	49.25	3.23	4.04

$C_{21}H_{38}N^+$: cetylpyridinium cation; $(C_6H_5)_4As^+$: tetraphenylarsonium cation